Syntheses and Crystal Structures of Tantalum(IV) Amido and Imido Halide Complexes

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The syntheses and crystal structures of monomeric tantalum(IV) amido halide and dimeric tantalum(IV) imido halide complexes are reported.

Recently, we reported the chemical vapour deposition of Ta_3N_5 thin films from $Ta(NMe_2)_5$ and ammonia at low temperatures.[1] We wish to use reduced tantalum amido and/or imido precursors in analogous chemical vapour deposition studies in the expectation that they will yield metal rich nitrides. Reduced tantalum amido and imido complexes are rare, however, consisting of only two reported Ta^{IV} complexes, $Ta(NMeBu^n)_4$ and the dimer $[Ta(\mu-H)_2-(cb)(PMe_2Ph)_2(H)]_2$ (cb = carbazole anion),[2] and Ta^{III} complexes of general formula $Ta(NR)XL_n$.[3] Herein, we report the preparation of new tantalum(IV) amido and imido halide complexes that are potential precursors in chemical vapour deposition studies, and which may be useful in the synthesis of other Ta^{IV} compounds.

$Ta[N(SiMe_3)_2]_2Cl_3$[4] in hexanes reacted with an excess of Na/Hg to give a deep-violet solution (4.5 h). The reaction mixture was filtered through Celite, concentrated and then cooled to $-35\,°C$. This produced very dark, almost black, crystals of $Ta[N(SiMe_3)_2]_2Cl_2$ in 64% yield.† The crystalline product was usually contaminated with a small amount (<5%) of $Ta[N(SiMe_3)_2]_2Cl_3$ even though an excess of Na/Hg was used. Attempts to prevent the contamination by using longer reaction times gave diminished yields and unidentified oily materials.

Thus far we have not been able to prepare $Ta[N(SiMe_3)_2]_2Cl_2$ directly from $LiN(SiMe_3)_2$ and $TaCl_4(py)_n$ or $TaCl_4(PMe_2Ph)_2$.[5] $Ta[N(SiMe_3)_2]_2Cl_2$ gives an ^1H NMR resonance that is broad and shifted, consistent with a paramagnetic compound.

A plot of $Ta[N(SiMe_3)_2]_2Cl_2$ from an X-ray crystallographic study is shown in Fig. 1.‡ In the structure, the $TaCl_2$ unit is disordered 50:50 over two sites related by a twofold axis, but only one $TaCl_2$ orientation of the disordered pair is shown in Fig. 1. There are two crystallographically distinct Ta–N distances as a consequence of the disorder.

The complex has a severely distorted tetrahedral geometry, which involves a 17° twist of the TaN_2 plane relative to the $TaCl_2$ plane such that the core has C_2 rather than C_{2v} symmetry. Also, the Cl–Ta–Cl angle is compressed [95.7 (2)°] and the N–Ta–N angle is opened [115.5(3)°] compared with normal tetrahedral angles. The Ta–Cl distances are normal but one Ta–N distance [1.899 (5) Å] is shorter than the other [2.027(5) Å]. The latter distance is significantly longer than the Ta–N distances in tbp $Ta[N(SiMe_3)_2]_2Cl_3$ [avg. 1.931(7) Å].[4] A space-filling plot suggests that the reason for the long Ta–N distance in $Ta[N(SiMe_3)_2]_2Cl_2$ is steric repulsion between the chlorines and two of the methyl groups on the N' amide ligand. Undoubtedly, the angular distortions of the $TaCl_2N_2$ core from tetrahedral are also caused primarily by steric interactions.

We have also prepared tantalum(IV) imido complexes. For example, reduction of Ta^V $Ta(NSiMe_3)[N(SiMe_3)_2]Cl_2(thf)$[6] in hexanes with 1.5 equiv. Na/Hg gave a dark-brown reaction mixture (3 h). The reaction mixture was filtered through Celite, concentrated and then cooled to $-35\,°C$. This produced dark-red crystals of $\{Ta(\mu-NSiMe_3)[N(SiMe_3)_2]Cl\}_2$ in 44% yield.† Yields of the dimer were lower when only 1 equiv. of Na/Hg or a longer reaction time was used in the synthesis.

The ^1H NMR spectrum of the dimer shows two singlets having normal chemical shifts, which is consistent with a diamagnetic compound. The singlet assigned to the amido ligand is broad at ambient temperature, but it sharpens as the temperature of the sample is raised, indicating hindered rotation about the $Ta-N(SiMe_3)_2$ bond.[7]

A plot of $\{Ta(\mu-NSiMe_3)[N(SiMe_3)_2Cl\}_2$ from a crystallo-
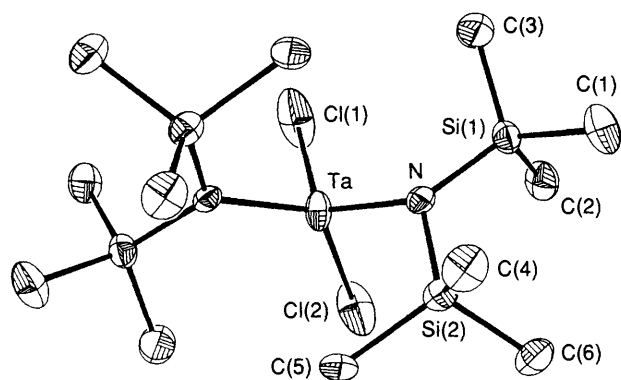

Fig. 1 Molecular structure of $Ta[N(SiMe_3)_2]_2Cl_2$. Bond distances (Å): Ta–Cl(1) 2.330 (6), Ta–Cl(2) 2.356 (6), Ta–N 1.899 (5), Ta–N' 2.027 (5). Bond angles (°): Cl(1)–Ta–Cl(2) 95.7 (2), Cl(1)–Ta–N 116.7 (2), Cl(2)–Ta–N' 129.5 (2), Cl(1)–Ta–N' 98.7 (2), Cl(2)–Ta–N 99.8 (2), N–Ta–N' 115.5 (3), Ta–N–Si(1) 125.3 (3), Ta–N–Si(2) 110.5 (3), Si(1)–N–Si(2) 120.0 (3).

† *Selected spectroscopic data.* $Ta[N(SiMe_3)_2]_2Cl_2$: ^1H NMR (C_6D_5) δ 7.5 (br). IR (Nujol, CsI, v/cm^{-1}) 1299w, 1257m(sh), 1245s, 1165w, 1139w, 888s, 847s, 789m, 703w, 667w, 642w, 619w, 400w, 387w, 337m, 308w. $\{Ta(\mu-NSiMe_3)[N(SiMe_3)_2]Cl\}_2$: ^1H NMR (C_6D_6) δ 0.57 (s, 18, μ-NSiMe_3), 0.32 (br s, 36, N(SiMe_3)$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6) 4.6 [s, N(SiMe_3)$_2$], 3.2 (s, μ-NSiMe_3). IR (Nujol, CsI, cm^{-1}) 1304w, 1246m, 1154w(br), 955m, 899m, 851m, 789w, 675w, 520w, 374w, 330w.
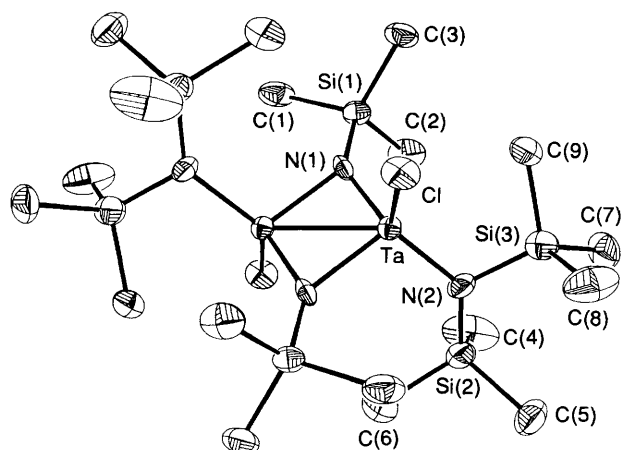
Fig. 2 Molecular structure of $\{Ta(\mu\text{-}NSiMe_3)[N(SiMe_3)_2]Cl\}_2$, 70% orientation. Bond distances (Å): Ta–Cl 2.320 (12), Ta–N(1) 1.994 (7), Ta–N(2) 2.045 (8), Ta–N(1') 1.985 (6), Ta–Ta' 2.621 (1). Bond angles (°): Cl–Ta–N(1) 112.1 (3), N(1)–Ta–N(2) 107.7 (3), N(1)–Ta–Ta' 48.6 (2), Cl–Ta–N(1') 99.3 (3), N(2)–Ta–N(1') 105.4 (3), Si(1)–N(1)–Ta' 129.9 (4), Cl–Ta–N(2) 129.2 (4), Cl–Ta–Ta' 114.1 (3), N(2)–Ta–Ta' 115.6 (3), N(1)–Ta–N(1') 97.6 (2), Ta'–Ta–N(1') 48.9 (2), Ta–N(1)–Si(1) 145.5 (4), Ta–N(1)–Ta' 82.4 (2), Ta–N(2)–Si(2) 138.5 (5), Ta–N(2)–Si(3) 100.3 (5), Si(2)–N(2)–Si(3) 120.7 (5).

graphic study is shown in Fig. 2.‡ The molecule is situated about an inversion centre, and the Ta and Cl atoms are disordered over two positions which refined to population factors of 70 and 30%. Overall, the molecular geometries in the two orientations are quite similar. The dimer has an edge-shared tetrahedral structure and a Ta–Ta distance, 2.621(1) Å, consistent with a metal–metal bond. The molecule appears to have a highly distorted amido ligand, possibly the result of steric interactions, but we hesitate to draw any firm conclusions because of the nature of the disorder in the crystal.

To our knowledge, $\{Ta(\mu\text{-}NSiMe_3)[N(SiMe_3)_2]Cl\}_2$ and $Ta[N(SiMe_3)_2]_2Cl_2$ are the first structurally characterized examples of Ta^{IV} imido and monomeric Ta^{IV} amido com-

plexes, respectively. The compounds $M[N(SiMe_3)_2]_2Cl_2$ (M = Zr, Hf),[8] which are d^0 congeners of d^1 $Ta[N(SiMe_3)_2]_2Cl_2$, are known, however, as are $[M(\mu\text{-}NBu^t)(NMe_2)_2]_2$ (M = Zr, Hf) dimers,[9] which are related to $\{Ta(\mu\text{-}NSiMe_3)[N(SiMe_3)_2]Cl\}_2$. Reactivity studies involving $Ta[N(SiMe_3)_2]_2Cl_2$, $\{Ta(\mu\text{-}NSiMe_3)[N(SiMe_3)_2]Cl\}_2$ and similar Ta^{IV} compounds, including chlorine substitution reactions, will be reported shortly.

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